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Flow-induced phase separation in polymer solutions

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Abstract. – A correct description of phase behaviour in polymer solutions requires a coupling between configurational statistics and thermodynamics. The effect of flow-induced chain deformation on the polymer-solvent interaction energy depends on the concentration and on the polymer architecture. It will be demonstrated, using thermodynamic arguments, that for linear polymers this may give rise to a large flow-induced demixing. For more complex architectures such as *ring* polymers and *branched* polymers, a maximum in the critical temperature *vs.* flow rate is predicted.

It is well known that flow can strongly influence the degree of mixing in polymer solutions and to a lesser degree in polymer blends. Experimental examples of flow-induced mixing as well as demixing are reported in the literature [1], [2]. For polymer solutions quite often shear-induced demixing, manifested by a large increase in scattering, is observed. Rangel-Nafaile *et al.* [1] reported shifts in the cloud points of high-molecular-weight polystyrene solutions in dioctylphtalate of the order of 20 °C or more as a function of flow rate. For low-molecular-weight solutions the effect seems to be strongly reduced and more complicated [3].

Theoretically, the influence of shear flow has been addressed in several ways. Assuming that the observed enhanced or reduced scattering corresponds to a change in the transition temperature of a genuine symmetry-breaking phase transition, a quasi-thermodynamic description was introduced by Ver Strate and Philippoff [4], and advanced in particularly by Rangel-Nafaile [1] and Wolf [5]. The approach is based on a Flory-Huggins–type description, including the influence of flow by a concentration-dependent stored free-energy term using a relation derived by Marrucci [6]. It has been criticized by Helfand and Fredrickson [7], Onuki [8] and others [9], because it has no clear basis in statistical mechanics.

The available experimental results and the theoretical descriptions based on the coupling between concentration fluctuations and stress indicate that entanglements are essential to obtain large shear-induced effects. For low-molecular-weight polymer solutions shear is supposed to suppress concentration fluctuations. The available experimental data [3] indicate that the

effect of shear is much smaller, and both reduced and enhanced concentration fluctuations are observed.

Weak elongational flow has been considered theoretically by Bhattacharjee *et al.* [10]. Using a continuum model for polymers with two- and three-body interactions, a theory was developed which predicts a flow-induced shift of the θ point to higher temperatures. It is related to the fact that the mean-squared radius of gyration is increased by the elongational flow. Because the repulsive three-body interactions depend more strongly on the monomer concentration than the two-body interactions, the repulsive interactions are reduced relative to the attractive interactions and the phase separation sets in at a higher temperature.

In this letter we consider again the influence of elongational flow on the phase behavior of polymer solutions. A quasi-equilibrium model will be proposed which is not restricted to weak flows. An important asset of our approach is the fact that the deformation of individual molecules is explicitly taken into account, thus providing a simple recipe to discuss the influence of the macromolecular architecture. This will be illustrated by comparing linear polymers with more complicated architectures such as ring and branched polymers.

Phase separation in polymer solutions is characterized by a strong asymmetry: a dilute phase of isolated partially collapsed polymer coils is in equilibrium with a semi-dilute solution. One of the most obvious effects of flow is the change of the polymer conformations. Due to the asymmetry, this will have a considerably different influence on the *interaction energy* in the dilute phase compared to the semi-dilute phase. In the dilute phase, the deformation (stretching) of isolated partially collapsed coils will result in a strong increase in polymer-solvent contacts. The semi-dilute regime on the other hand is characterized by a more homogeneous segment distribution for which deformation of the chains will increase the number of polymer-solvent contacts to a much lesser degree.

This effect can be most easily discussed employing a quasi-equilibrium description. To this end, the issue of an effective potential governing the behaviour of non-equilibrium systems and the explicit consideration of a conformation-dependent number of polymer-solvent contacts will be addressed first. The Flory-Huggins theory estimates the number of polymer-solvent contacts ignoring chain connectivity and is obviously inadequate to describe even phase behaviour of quiescent polymer solutions. This issue was considered several years ago by one of us [11] and an alternative model was introduced. It has subsequently been applied to various problems involving polymer solutions and shown to remedy several shortcomings of the Flory-Huggins approach [12]. The issue of an effective potential governing the behaviour of a polymer solution under flow was first raised by Kramers [13]. He considered a dilute polymer solution under flow. Assuming free-draining conditions, the force $\mathbf{F}_i$ on bead i in a flowing fluid is given by

$$\mathbf{F}_i = -\zeta(-\mathbf{v}_i' + \mathbf{v}_i'') + \mathbf{F}_i' \,. \tag{1}$$

Here $\mathbf{v}_i'$ and $\mathbf{v}_i''$ are the velocities of the fluid at the position of the bead and of the bead itself, respectively, ζ is the friction coefficient and $\mathbf{F}_i'$ is a random force. Now, suppose the flow is irrotational, *i.e.* $\boldsymbol{\nabla} \times \mathbf{v}'(\mathbf{r}) = 0$, then the velocity follows from a velocity potential: $\mathbf{v}'(\mathbf{r}) = -\nabla\psi(\mathbf{r})$. Introducing the potential energy $U(\mathbf{r}) = \zeta\psi(\mathbf{r})$ then gives

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i} - \zeta\dot{\mathbf{r}}_i + \mathbf{F}_i' \,. \tag{2}$$

Hence, the equations of motion are the same as those which would apply to polymer beads in a liquid at rest if it were subject to a force field with potential U.

In the case of shear flow given by $(u = \dot{\gamma}y, v = 0, w = 0)$, the flow is not irrotational and can be decomposed in an irrotational part $(u = \frac{1}{2}\dot{\gamma}y, v = \frac{1}{2}\dot{\gamma}x, w = 0)$ and a uniform rotation given by $(u = \frac{1}{2}\dot{\gamma}y, v = -\frac{1}{2}\dot{\gamma}x, w = 0)$.

Here we will restrict ourselves to the irrotational, *i.e.* elongational part of the flow, which has the strongest effect on the polymer conformations. Furthermore, free draining conditions will be assumed. Under these assumptions the flow follows from a velocity potential given by

$$\psi(\mathbf{r}) = -\frac{1}{2}\dot{\gamma}xy\,. \tag{3}$$

For a polymer chain with conformation α this implies an additional potential energy given by

$$U(\alpha) = -\frac{1}{2}\zeta\dot{\gamma}\sum_{i=1}^{N} x_i(\alpha)y_i(\alpha)\,, \tag{4}$$

where x_i (y_i) is the $x(y)$-coordinate of bead i with respect to the center of mass of the molecule; N is the number of beads per chain.

Our equilibrium model follows now simply by adding this potential energy term to the expression introduced by Szleifer [11]. This implies that the starting point of our approach is given by

$$\begin{aligned}\beta F = n_{\mathrm{s}}\ln\phi + n_{\mathrm{p}}\ln(1-\phi) + n_{\mathrm{p}}\sum_{\alpha}P(\alpha)\ln P(\alpha) + \\ + n_{\mathrm{p}}\chi\phi\sum_{\alpha}P(\alpha)n_{\mathrm{e}}(\alpha) + n_{\mathrm{p}}\sum_{\alpha}P(\alpha)U(\alpha)\,,\end{aligned} \tag{5}$$

where $\beta = 1/kT$; n_{s} and n_{p} are the number of solvent and polymer molecules, respectively, ϕ is the volume fraction of solvent and $P(\alpha)$ is the probability to find a polymer molecule in a conformation α with $n_{\mathrm{e}}(\alpha)$ external contacts. The number of external contacts is defined as all non-bonded contacts minus the intra-molecular contacts (further on, we will restrict ourselves to a cubic lattice model where contacts are well defined).

This expression is not difficult to understand: the first two terms represent the translational entropies and the third term the conformational entropy. The fourth term is the interaction energy assuming that the probability that an external contact is a contact with a solvent molecule is given by the mean-field value ϕ. The last term represents the potential energy due to the elongational flow. The χ-parameter is defined by $\chi = \frac{\Delta\epsilon}{kT}$, where $\Delta\epsilon = \epsilon_{\mathrm{ps}} - \frac{1}{2}(\epsilon_{\mathrm{pp}} + \epsilon_{\mathrm{ss}})$; it differs from the familiar Flory-Huggins parameter by the absence of a factor $z-2$ corresponding to the number of external non-bonded contacts per segment (z is the lattice coordination number). Equation (5) expresses the free energy as a function of the probability $P(\alpha)$. An expression for $P(\alpha)$ can be found by minimization: $\delta F(\alpha)/\delta P(\alpha) = 0$, leading to

$$P(\alpha) = \frac{\exp\left[-\chi\phi n_{\mathrm{e}}(\alpha) + \beta U(\alpha)\right]}{q}\,, \tag{6}$$

where q is the normalization constant. This results in the following simple form for the free energy:

$$\beta F = n_{\mathrm{s}}\ln\phi + n_{\mathrm{p}}\ln(1-\phi) - n_{\mathrm{p}}\ln q\,. \tag{7}$$

Here, the coupling between chain statistics, flow field and thermodynamics is present in q. The familiar spinodal expression, critical point conditions and phase equilibria conditions can be used in conjunction with this expression to determine the phase diagram. The corresponding equations for the critical point are

$$\frac{1}{\phi} + \frac{1}{N(1-\phi)} - \frac{2}{N}\chi\langle n_{\mathrm{e}}\rangle - \frac{1-\phi}{N}\chi^2[\langle n_{\mathrm{e}}^2\rangle - \langle n_{\mathrm{e}}\rangle^2] = 0\,, \tag{8}$$

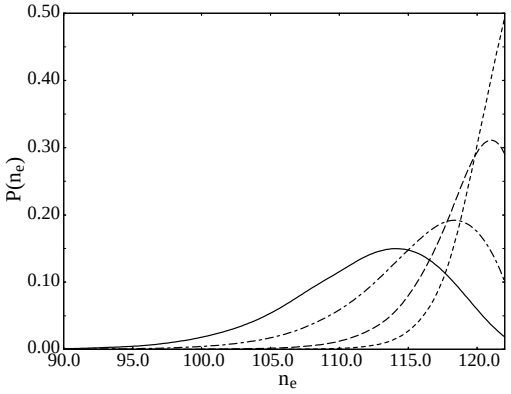

Fig. 1

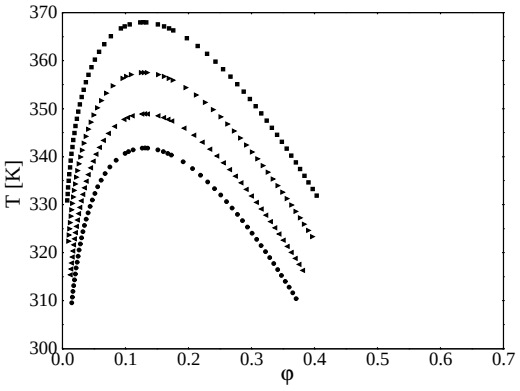

Fig. 2

Fig. 1. – Distribution function $P(\alpha)$ of the number of external contacts n_e as a function of flow rate for isolated linear chains of length $N = 30$ under athermal conditions. Solid line: zero flow, · – · – $\dot{\gamma}\tau = 36.5$, – – – $\dot{\gamma}\tau = 73.0$ and $\cdots$ $\dot{\gamma}\tau = 97.3$.

Fig. 2. – Phase diagrams as a function of flow rate for linear chains of length $N = 60$. • zero flow, ◀ $\dot{\gamma}\tau = 31.0$, ▶ $\dot{\gamma}\tau = 40.3$ and ■ $\dot{\gamma}\tau = 47.0$.

$$-\frac{1}{N(1-\phi)^2}+\frac{1}{\phi^2}-\frac{3}{N}\chi^2[\langle n_e^2\rangle-\langle n_e\rangle^2]- \\ -\frac{1-\phi}{N}\chi^3[\langle n_e^3\rangle-3\langle n_e\rangle\langle n_e^2\rangle+2\langle n_e\rangle^3]=0\,, \tag{9}$$

where

$$\langle A\rangle=\sum_\alpha P(\alpha)A(\alpha)\,. \tag{10}$$

Similar equations can be derived for the coexistence curve [11].

In the case of a quiescent solution this formalism predicts a strong reduction in the critical temperature compared to the simple Flory-Huggins result [11]. If an additional potential (eq. (4)) is present, the stretched conformations become more favourable. Consequently, for linear polymers $n_e(\alpha)$ will approach its maximum value $n_e^{\max} = N(z-2)+2$ and the fluctuations in the number of external contacts will gradually disappear. Hence, the phase boundary will shift back towards the Flory-Huggins prediction implying flow-induced demixing.

To illustrate the influence of the potential (eq. (4)) on the distribution of external contacts, Monte Carlo simulations were performed using the slithering snake algorithm [14] together with the Metropolis scheme [15]. Isolated chains were simulated under athermal solvent conditions. Figure 1 shows the results for relatively short linear chains $N = 30$ as a function of $\dot{\gamma}\tau$, where $\tau = \frac{\zeta a^2 N^2}{kT}$. τ corresponds to the longest relaxation time of a Rouse molecule of N segments, a situation that corresponds to θ conditions, *i.e.* close to the critical point. The figure demonstrates the essential features: increasing $\langle n_e\rangle$ and narrowing of the distribution. For high shear rates, the coil really stretches and $\langle n_e\rangle$ approaches its maximum value. Furthermore, the second- and third-order fluctuations in n_e diminish as can be seen from data gathered in table I.

To calculate the phase diagram, a representative ensemble of conformations has to be generated, which is accomplished by generating a large number (order 10^6) of self-avoiding

TABLE I. – *The three moments of the number of external contacts as a function of the flow rate for isolated linear chains of length $N = 30$ under athermal conditions.*

$\dot{\gamma}\tau$	$\langle n_e \rangle$	$\langle n_e^2 \rangle - \langle n_e \rangle^2$	$\langle n_e^3 \rangle - 3\langle n_e^2 \rangle \langle n_e \rangle + 2\langle n_e \rangle^3$
0.0	111.95	31.45	−130.97
24.3	112.79	30.05	−131.84
36.5	113.99	27.65	−131.35
48.6	115.76	22.46	−116.69
60.8	117.56	15.42	−80.62
73.0	118.93	9.539	−42.45
97.3	120.38	4.211	−13.69

walks of length N on a cubic lattice using the Rosenbluth-Rosenbluth scheme [16]. For the present study each conformation consisted of 60 segments, *i.e.* $N = 60$. In all calculations $\Delta\epsilon/k = 65.0$ K was used. Figure 2 shows the corresponding phase diagrams. Clearly, for stronger elongational flows the critical point shifts to higher temperatures implying flow-induced demixing. The difference in critical temperature between no-flow and strongest flow considered is approximately 25 °C. (Preliminary data indicate that this value depends only slightly on N.) The critical point shifts somewhat to lower polymer concentrations. The highest flow rate employed corresponds to $\dot{\gamma}\tau = 47.0$. For still stronger elongational flows the statistics of our method becomes extremely bad due to the high probability of extended conformations, which are not accurately represented in the ensemble of 10^6 self-avoiding walk conformations. Increasing the number of conformations will not improve the situation very much.

One of the obvious advantages of our approach is the simple way in which the influence

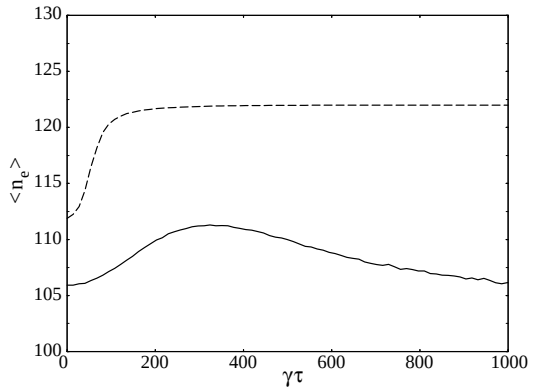

Fig. 3. – Average number of external contacts $\langle n_e \rangle$ as a function of $\dot{\gamma}\tau$ for an isolated linear polymer (– – –) and an isolated ring polymer (—). Chain length $N = 30$ and athermal conditions.

of the polymer architecture can be considered. To illustrate this, we will briefly consider a ring polymer solution. In this case the influence of the deformation of the polymer coil on the probability distribution for the number of external contacts is more complex. Figure 3 shows a comparison between the average number of external contacts of a self-avoiding linear polymer and a self-avoiding, topology-conserving, ring polymer as a function of the flow strength. Interestingly, the number of external contacts of the ring polymer first increases but then decreases again at very strong elongational flows because of an increased number of intramolecular contacts. The same phenomenon should obviously occur for branched polymers. As a consequence, the phase behavior predicted on the basis of eq. (5), first shows an increased critical temperature (flow-induced demixing) followed by a decrease in critical temperature. This effect seems real, although it should be realised that the mean-field assumption used for the probability that an external contact of a polymer molecule is with a solvent molecule is expected to become less accurate for strongly elongated conformations. For ring polymers there is the additional complication of intermolecular topological interactions.

Our formalism demonstrates that the effect of the inherent asymmetry of polymer solutions on the interaction energy can be a very important factor in the influence of flow on phase behavior. A close relation exists between the number of intramolecular interactions, the deformation of the polymer coil and the polymer chain architecture. Where linear polymers are predicted to exhibit flow-induced demixing only, more complex architectures, such as ring polymers but also branched molecules, are expected to show more complicated behavior characterised by a maximum in the critical temperature as a function of flow rate. The discussion was restricted to elongational flow, but the specific interaction features, that formed the basis for this article, will be important for shear flow as well. Hence, the next challenge is to incorporate these in a dynamical theory of concentration fluctuations.

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